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Review Article

Decomposition and formation of magnesium borohydride

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ARTICLE INFO

Article history:
Received 12 March 2016
Received in revised form
1 May 2016
Accepted 5 May 2016
Available online 26 May 2016

Keywords:
Tetrahydroborate
Reversible hydrogen sorption
Nanotechnologies
Fuel cell
Secondary battery

ABSTRACT

Nowadays, among all known borohydrides magnesium borohydride, $Mg(BH_4)_2$, is the only one that demonstrates a partial reversible hydrogen sorption in moderate conditions. This is a clear reason why composites based on $Mg(BH_4)_2$ are extensively studied fundamentally and are applicable as hydrogen storage materials. The review summarizes the main challenges still present for $Mg(BH_4)_2$ that are decomposition and formation providing for the practical use of hydrogen mobility. Some technological approaches to the development of nanocomposites based on $Mg(BH_4)_2$ are considered and discussed. Profound conclusions and future application of nanocomposites in fuel cells and secondary batteries is the final item of the proposed work.

Contents

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http://dx.doi.org/10.1016/j.ijhydene.2016.05.062

Introduction

Chemistry of metal borohydride (tetrahydroborate) complexes has shown a strong interest in electron structure and bonding between metallic atoms and borohydrido ligands [1–3] since these compounds frequently find new applications. Research activity for the inorganic complexes started with transition metal borohydrides when their synthesis and practical application in catalysis was concerned [4]. Later rare earth metal borohydrides came to be used mainly for polymerization reactions [5]. A decade ago alkaline and alkaline earth metals borohydrides attracted attention as hydrogen storage materials [6–10] due to their high hydrogen content.

Magnesium borohydride (MBH) is one of the most well-studied complex hydrides nowadays since its properties encourage many scientists to find a solution for reversible hydrogen storage. The first records on MBH were dedicated to its chemical synthesis [11], and the nature of the bonding and coordination mode of the $(BH_4)^-$ ligand was of a great interest [12]. A fascinating aspect of the MBH's crystal structure is its rich polymorphous crystallographic complexity that is not observed for tetragonal $Be(BH_4)_2$ and orthorhombic $Ca(BH_4)_2$. The increase in the hydrogen coordination number from six (for Be^{2+}) to eight (for Mg^{2+}) and twelve (for Ca^{2+}) suggests that cation size is one of the reasons why MBH does not adopt one of the simpler structures of its alkaline-earth analogs. The similarity of γ-phase of MBH frameworks to MOFs provides a route towards novel hybrid materials: combined use of $(BH_4)^-$ ions with other directional ligands may produce new porous materials, with high gas adsorption enthalpy and selectivity of absorption. It is remarkable that porous MBH contains a large amount of hydrogen (~14.9 wt% H_2) chemically bonded to boron and stores additional (~3.0 wt% H_2) physically adsorbed hydrogen at low temperatures. Bulk MBH demonstrates multi-step decomposition with some intermediates, mainly higher *closo*-borates, although among other alkaline earth metal borohydrides only MBH allows to expect hydrogen reversible sorption, with MgB_2 as the main decomposition product. It is believed that using modern nanotechnologies the hydrogen storage materials based on MBH can meet the basic requirements for being used in fuel cells. From the thermodynamic point of view, their decomposition in moderate conditions (from −25 to +50 °C; ≤100 bar H_2) means reaction enthalpy around ~25–35 kJ/mol H_2. The sorption must be reversible (~90%) and have fast kinetics (<5 min) during at least 500 cycles.

The present review summarizes the main topical issues: (i) crystal structure and thermodynamic properties, (ii) decomposition and (iii) synthesis of MBH as well (iv) development of its nanocomposites for fast and reversible hydrogen storage. Well-grounded conclusions and future outlooks of promising MBH nanocomposites to be applied in fuel cell and batteries are the final key item of the proposed work.

Crystal structure and thermodynamic properties of magnesium borohydride

The first studies of the crystal structure of solvent-free MBH was proposed in the early 1960s [13]. Later the group of V.N. Konoplev suggested the existence of two crystalline modifications of MBH as a tetragonal low-temperature phase and a cubic high temperature phase [14,15]. Since that time both experiments and theoretical works have been pointing to immense polymorphism of MBH. Currently, five crystal structures of MBH have been experimentally identified and each of them is characterized by its own thermodynamic properties.

Polymorphism

A highly crystalline MBH was obtained and used for high-resolution diffraction studies in Ref. [16]. The structure was identified and refined on the basis of the data measured during synchrotron X-ray and neutron diffraction experiments on a multiphase powder sample (containing ca. 50 wt% of the main phase). The complexity of the structure had never been known before for this type of compounds and, in contrast to previous reports, the structure of MBH was designated to hexagonal symmetry with the $P6_1$ space group. The structure contained five symmetry-independent Mg^{2+} ions and ten symmetry-independent $(BH_4)^-$ ions, therefore the Mg^{2+} and $(BH_4)^-$ ions were connected into a novel three-dimensional framework. It was proposed that each Mg^{2+} ion was surrounded by four $(BH_4)^-$ tetrahedra arranged in a deformed tetrahedron while each $(BH_4)^-$ ion was approximately linearly coordinated by two Mg^{2+} ions. The $(BH_4)^-$ tetrahedra was oriented so that each Mg^{2+} ion was coordinated by tetrahedral edges only (called μ_2-H_2 bridges), this resulting in an unusual eightfold, relatively irregular hydrogen coordination environment. It was concluded that "magnesium" network ($4.6 \leq Mg\cdots Mg \leq 5.0$ Å) locally resembled an amorphous state, with respect to both complexity and local environments of numerous building units.